

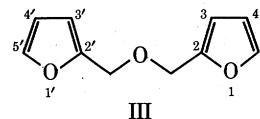
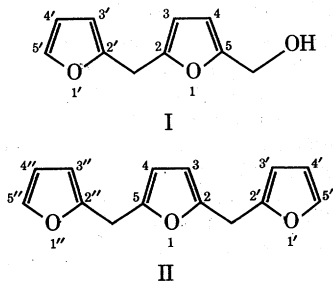
## Mass Spectrometry of Three Furanic Compounds Containing Two or Three Furan Nuclei

Low-resolution mass spectra and high-resolution data are presented and discussed for the following compounds: [(5-hydroxymethyl-2-furyl)-(2'-furyl)]methane (I), [2-(2'-furfuryl)-5-(2''-fur-

furyl)]furan (II), and difurfuryl ether (III). Observed metastable ions are indicated as support for the proposed fragmentations.

Mass spectrometry is an important tool for the elucidation of the structure of natural products and of flavor constituents (Kolor, 1972). Furanic compounds from carbohydrate degradation are often found in foods and food-related model systems (Hodge, 1967; Ferretti *et al.*, 1970). Whereas a reasonable amount of published data on electron-impact induced fragmentation of certain classes of furanic compounds is available (Porter and Baldas, 1971), very little correlated mass spectral information exists for compounds containing more than one furan nucleus (Budzikiewicz *et al.*, 1967; Porter and Baldas, 1971). Compounds having two or three furan nuclei have been identified in roasted coffee beans (Stoll *et al.*, 1967; Stoffelsma *et al.*, 1968), in popcorn (Walradt *et al.*, 1970), and in heated whey powder (Ferretti and Flanagan, 1971b). We previously reported (Ferretti *et al.*, 1974) mass spectral characteristics of four acyl derivatives of 2,2'-difurfylmethane in the hope that they may be of use to other investigators in identifying such compounds and structurally related ones.

This investigation is the continuation of our previous work, and deals with high-resolution measurements of the following compounds.



These compounds have been identified in a (milk-related) lactose-casein browning system (Ferretti and Flanagan, 1971a). The ether III and the trifuranic compound II have also been found in an *N* $\alpha$ -formyl-L-lysine-D-lactose model system (Ferretti and Flanagan, 1973) and/or in heated whey powder (Ferretti and Flanagan, 1971b).

### EXPERIMENTAL SECTION

For gas chromatography-mass spectrometry an LKB 9000 instrument and the same conditions previously described (Ferretti *et al.*, 1974) were used. The high-resolution mass spectra (resolution *ca.* 10,000) were determined with a CEC 21-110B instrument at 70 eV and an ion source temperature of 150°. Sample introduction, exact mass measurements, and calculations were performed as described previously (Ferretti *et al.*, 1974). The metastable ions were observed in the photographic charts from the LKB spectrometer.

The three compounds were synthesized and purified as reported earlier (Ferretti and Flanagan, 1971a).

### RESULTS AND DISCUSSION

The mass spectra and elemental compositions of important ions of the following compounds are shown in Figure 1: [(5-hydroxymethyl-2-furyl)-(2'-furyl)]methane (I), [2-(2'-furfuryl)-5-(2''-furfuryl)]furan (II), and difurfuryl ether (III). Scheme I illustrates the possible fragmentation processes for compounds I and II, and Scheme II illustrates the degradation of III. In both schemes the observed metastable transitions are indicated by asterisks.

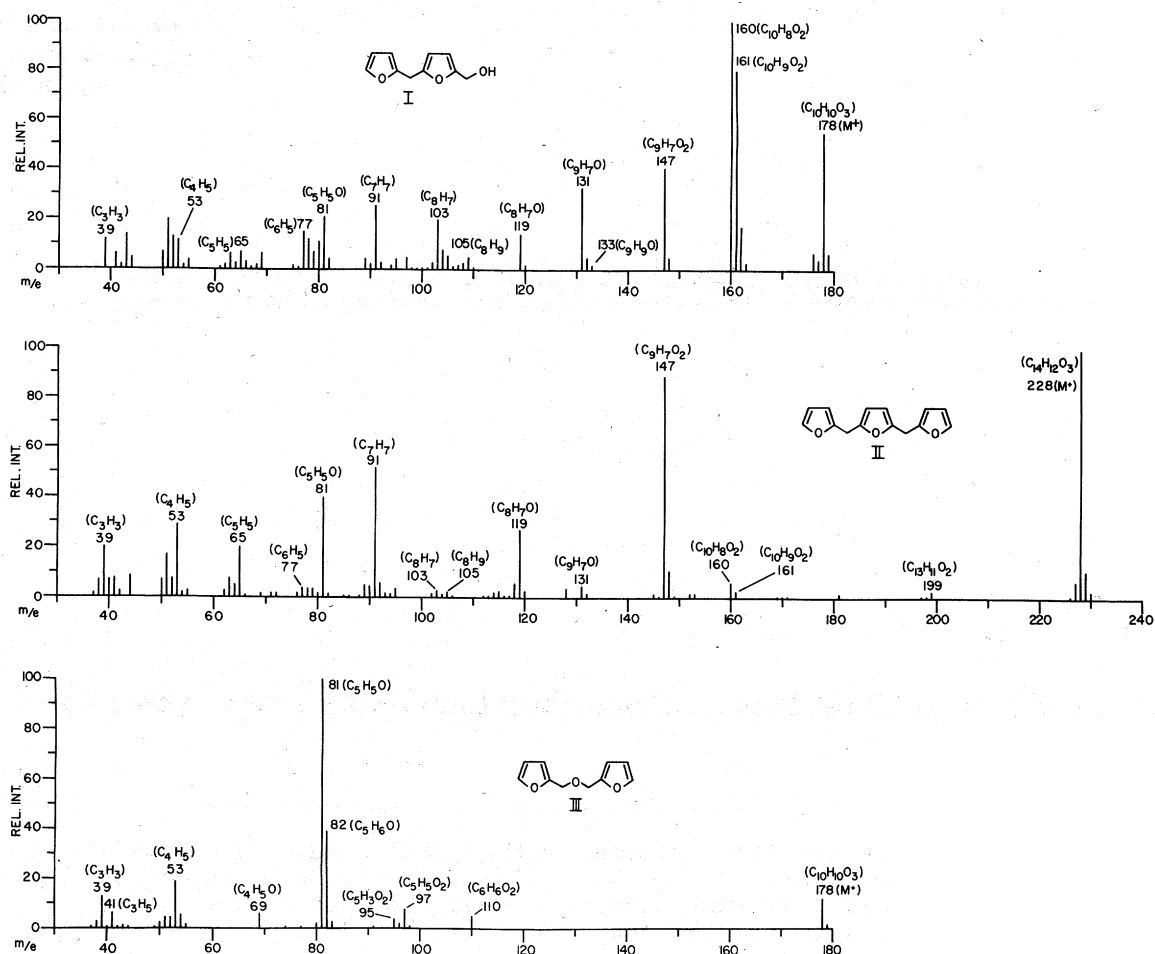
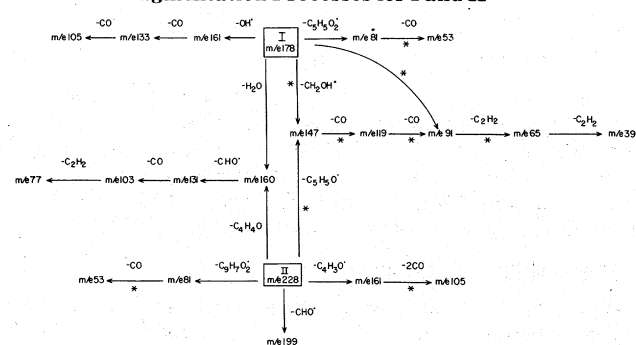
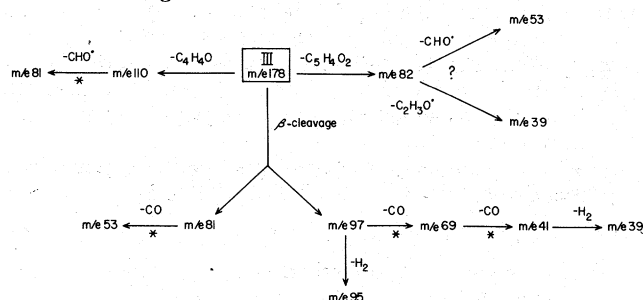


Figure 1. Mass spectra of compounds I, II, and III.

#### Scheme I. Fragmentation Processes for I and II



#### Scheme II. Fragmentation Processes for III



The mass spectra of I and II can be compared with those of the acyl derivatives of 2,2'-difurylmethane (Ferretti *et al.*, 1974). Their similarity is remarkable both in terms of the presence of ions at specific  $m/e$  values and of mode of fragmentation primarily consisting of successive

eliminations of CO and ethylene. The major fragmentation pathways in I are those initiated by the loss of the hydroxymethyl radical ( $M^+ \rightarrow m/e 147$ ) and of one molecule of water ( $M^+ \rightarrow m/e 160$ ). The major fragments in the spectrum of II result from an  $\alpha$  cleavage relative to the center furan nucleus with the charge unevenly distributed between the  $[C_9H_7O_2]^+$  species ( $m/e 147$ ) and the  $m/e 81$  fragment which is probably the pyrilium ion (Budzikiewicz *et al.*, 1967). Of the two minor pathways for the fragmentation of II, one is initiated by the loss of a furyl radical ( $M^+ \rightarrow m/e 161$ ); the other pathway, which results in the rearrangement ion of  $m/e 160$ , is triggered by the elimination of the elements of a neutral furan molecule with attendant hydrogen rearrangement. The elimination of  $CHO\cdot$  from the molecular ion of II is analogous to the previously observed (Ferretti *et al.*, 1974) elimination of an acetyl radical from [(5-acetyl-2-furyl)-(5'-methyl-2'-furyl)]methane and from [(5-formyl-2-furyl)-(5'-methyl-2'-furyl)]methane involving the furan oxygen.

The mass spectrum of III is characterized by the  $m/e 81$  and 97 fragments probably resulting, at least in part, from simple  $\beta$  cleavage, and by the two rearrangement ions of  $m/e 82$  and 110. The latter results from the molecular ion by elimination of the elements of furan. A similar elimination was observed in the spectrum of II (*vide supra*). One of the plausible explanations for the presence of the ion of  $m/e 82$  in the spectrum of III is the occurrence of a  $\beta$  cleavage with concomitant hydrogen transfer and expulsion of the elements of furfural. This mode of fragmentation is frequently encountered in ethers (Budzikiewicz *et al.*, 1967). If the  $[C_9H_6O]^+$  species has the structure of methylfuran, then it can eject a  $CHO\cdot$  ( $m/e 82 \rightarrow m/e 53$ ) or an acetyl radical ( $m/e 82 \rightarrow m/e 39$ ) as shown in Scheme II.

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